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Prediction of Photochemical Transformation of Pollutants in the Aquatic Environment

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ABSTRACT

Mathematical models that predict concentration-time profiles can be used to assess potential exposure of aquatic organisms to toxic pollutants. Such models integrate quantitative descriptions of individual transport and transformation processes that affect pollutant behavior in the environment. Discussion in this paper focuses on methods for prediction of one important transformation process, photolysis by the action of sunlight.

Two general classes of photochemical transformation are direct photolysis, initiated by direct absorption of light by the pollutant, and indirect or sensitized photolysis involving light absorption by natural "photosensitizers." At concentrations normally encountered in natural waters, direct photolysis is described by first order rate expressions. Equations that employ solar irradiance, quantum yields, and absorption spectra of pollutants are used to predict photolysis rates as a function of time of day, season, location, and water depth. Sensitized photolysis can proceed by a variety of mechanisms including energy transfer, sensitizer-pollutant reaction, and oxidation involving singlet oxygen or free radicals. Recent studies have indicated that singlet oxygen, a species that rapidly oxidizes certain pollutants such as polycyclic aromatics, is generated photochemically in a variety of natural waters. Although qualitative evidence indicates that other types of sensitized photolysis are important, mechanisms and equations required for quantitative description of these processes are still poorly defined.

INTRODUCTION

The time-honored approach for deducing the environmental fate of a man-made chemical has been to study its behavior under field conditions. Usually, the approach has involved collecting and analyzing large numbers of samples from a portion of the environment, such as a river or field, that has been exposed to the chemical. To complement this approach, qualitative laboratory studies are used to explain the observed field behavior.

Carefully planned field studies still remain the best way for evaluating the behavior of chemicals in the environment. Public concern over the toxicity and adverse ecological effects of certain chemicals, however, has stimulated interest in predicting which chemicals might cause harm to susceptible organisms. Because few field data on these compounds may be available, initial decisions concerning their environmental safety will be based largely on laboratory data. To adequately assess the potential hazard of chemicals to aquatic organisms, toxicity data must be accompanied by some way of predicting the persistence and movement of the chemicals in aquatic ecosystems. Two laboratory approaches appear most promising. One, discussed elsewhere (Ref. 1), involves observing the distribution of chemicals when added to small model ecosystems. The other approach uses laboratory data concerning various environmental processes that determine the transport and transformation of chemicals in the aquatic environment. During the past few years, our research program has developed techniques for extrapolating quantitative data concerning microbial, hydrolytic, photochemical, and sorption processes from laboratory to environmental conditions (Ref. 2). We have used these techniques to assess the likely importance of various environmental pathways for degradation of chemicals (Ref. 3). Recently, Hill and coworkers (4) and Smith *et al.* (5) have shown how quantitative laboratory data concerning toxic chemicals can be integrated in mathematical models to predict concentration-time profiles in various environmental compartments. This paper is concerned with laboratory procedures for forecasting the photochemical transformation of chemicals in the aquatic environment.

Energy from the sun is the primary driving force for degradation of chemicals in the aquatic environment. It is well-recognized that solar energy stored in biological systems may eventually be used to transform natural and man-made chemicals. The chemical structures of synthetic chemicals, however, are often very different from those of natural substances. Thus, considerable periods of time may be required for acclimation and subsequent degradation of these chemicals to occur by biological pathways. However, other non-biological pathways for transformation are also available. Sunlight absorbed by the atmosphere and water bodies indirectly provides the energy for spontaneous, thermal reactions such as hydrolysis and oxidation (Ref. 6). Finally, the simplest pathway for degradation involves the direct conversion of absorbed solar energy into photochemical reaction. The most obvious evidence of photoreaction in aquatic environments is the widespread presence of phytoplankton and other light-dependent underwater plants. Much effort has been directed towards mathematically describing photosynthesis by freshwater and marine phytoplankton (Ref. 7), but most of this work is not directly applicable to predicting photochemical reaction of synthetic chemicals.

Any photochemical reaction depends upon the dose of light received and the response of the irradiated system. Most of our discussion here centers upon prediction of the response of chemicals in those portions of aquatic environments that are exposed to sunlight. Later in this paper, we will discuss factors affecting the dose of light received by pollutants and outdoor verification of the predictions based on laboratory data.

PATHWAYS FOR PHOTOLYSIS IN AQUATIC ENVIRONMENTS

A number of competing photochemical pathways may determine the response of a chemical exposed to sunlight. For convenience, we have subdivided these various pathways into two general classes of photoreaction, direct photolysis and indirect or sensitized photolysis.

Direct Photolysis

Theory and equations. The simplest mechanism for photolysis involves direct absorption of light, which produces a molecule in an electronically excited state (eq. 1). The excited molecule either reacts (eq. 2) or decays by some mechanism back to its ground state (eq. 3).

$$P_o + \text{Light} \longrightarrow P^* \quad (1)$$

$$P^* \xrightarrow{k_2} \text{Products} \quad (2)$$

$$P^* \xrightarrow{k_3} P_o \quad (3)$$

Most studies of aquatic pollutants have involved elucidation of products derived from direct photolysis in non-absorbing solvents such as water, methanol, or hexane.

The mere passage of light through a system does not ensure direct photolysis. The light must be of wavelengths that correspond to electronic absorption by the chemical. Thus, it is entirely possible that a pollutant that reacts rapidly under sunlight could be unreactive when exposed to a lamp with footcandle intensity similar to that of sunlight. Units of luminosity such as footcandles refer to visible light, whereas many pollutants absorb only the ultraviolet (uv) portion of sunlight. On the other hand, chemicals such as DDT that photoreact rapidly when exposed to uv light from mercury or xenon lamps (even with filtering by Pyrex) can be very unreactive outdoors because of a lack of sunlight absorption (Ref. 8).

Clearly, the rate* of direct photolysis is related to the rate I_a at which light is absorbed by the pollutant. Under most natural conditions, the concentration of a pollutant [P] is very low and I_a is directly proportional to [P] (Ref. 9). The proportionality constant, k_a, is expressed in units of reciprocal time and is called the

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* The rate of photolysis is defined as the change in concentration per unit of time, -d[P]/dt.

specific sunlight absorption rate. The value of k_a can be calculated using solar irradiance incident on the surface of the water body, absorption coefficients of the pollutant, and attenuation coefficients of the water body (Ref. 9).

If all of the light absorbed by the pollutant were converted into photoreaction, the photolysis rate would simply equal I_a. In fact, usually only a fraction of the absorbed light causes chemical change. This fraction is called the quantum yield for reaction, ϕ. The rate expression for direct photolysis is thus:

$$-\frac{d[P]}{dt} = I_a \phi = k_a \phi [P] = k'[P] \quad (4)$$

To make the data easier to visualize, we also have expressed them in terms of half-lives inherent to direct photolysis, $t_{\frac{1}{2}}$:

$$t_{\frac{1}{2}} = \frac{0.693}{k'} \quad (5)$$

The value of k_a in a water body depends strongly on light screening by natural substances in the water. The screening effect will be discussed later in the paper. Near the surface of a water body, the pollutant is completely exposed to sunlight and k_a becomes independent of the optical properties of the water body. The near-surface half-life, $t^\circ_{\frac{1}{2}}$, can be computed by eq. (6):

$$t^\circ_{\frac{1}{2}} = \frac{1.81 \times 10^{28}}{\phi \Sigma \epsilon_\lambda Z_\lambda} \quad (6)$$

where ϵ_λ is the molar absorptivity of the pollutant in 1 $mole^{-1}$ cm^{-1} at wavelength λ, Z_λ is solar irradiance at a wavelength interval centered at λ in photons cm^{-2} sec^{-1}, and the term $\Sigma\epsilon_\lambda Z_\lambda$ indicates summation over the wavelengths of sunlight absorbed by the pollutant. Tables of Z_λ values have been published elsewhere (Ref. 9). Molar absorptivities, or "extinction coefficients," can be easily obtained with modern spectrophotometers; mixtures of water and acetonitrile or methanol can be used as solvents for these determinations when solubility limitations in water are a problem. Zepp (10) has recently described procedures for measuring quantum yields for reaction of pollutants in very dilute aqueous solution.

Predicted direct photolysis rates. Zepp and Cline (9) have developed a computer program that is used to calculate solar spectral irradiance as a function of time-of-day, season, and latitude. The program uses solar irradiance, quantum yields, and eq. (4) to compute direct photolysis rates of pollutants in water bodies. Results of the computations for the widely distributed pollutant, benzo[a]pyrene, illustrate how direct photolysis varies with time and location (Fig. 1 and 2). Molar absorptivities and quantum yields obtained by Smith and coworkers (5) were used in these computations. Seasonal variations are predicted to be more pronounced in Europe (latitude 50°N) than in the mid-U.S. (latitude 40°N), but during the summer months, there is not much difference in half-life (Fig. 1). Changes in photolysis rates are caused by fluctuations in solar irradiance as well as by

variations in the period of daylight (Fig. 2). To facilitate comparison of photolysis to other processes that are not light-dependent, the data in Fig. 1 are integrated over the 24-hour day (Ref. 3). Data summarized in Table 1 indicate that many chemicals are rapidly transformed upon exposure to sunlight.

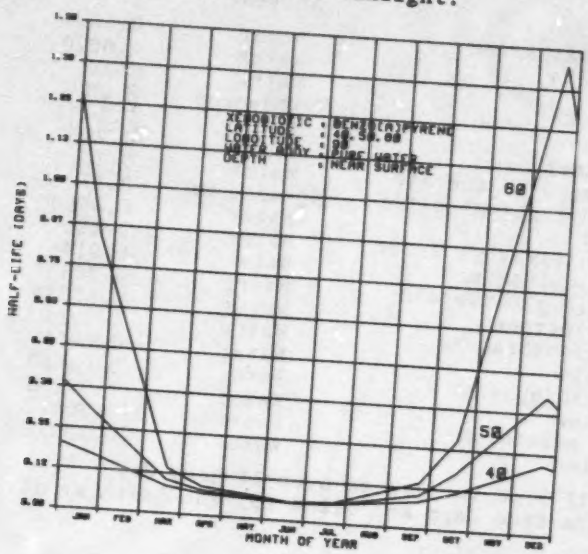


Fig. 1 Annual variation of the near-surface half-life ($t_{\frac{1}{2}}$) of benzo[a]pyrene at several Northern latitudes

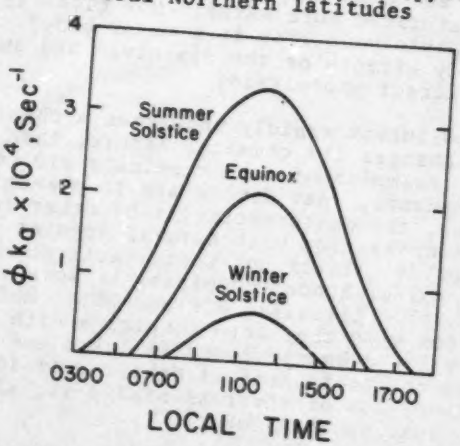


Fig. 2 Diurnal variation in direct photolysis rate of benzo[a]pyrene computed for Amsterdam, The Netherlands

TABLE 1 Predicted Near-surface Half-lives, $t_{\frac{1}{2}}^{\circ}$, for Direct Photolysis of Pesticides and Polycyclic Aromatic Hydrocarbons - Midsummer, Latitude 40°N [a,b]

Chemical	Solvent	Quantum Yield for Reaction	$t_{\frac{1}{2}}^{\circ}$, days
(1) N-Nitrosoatrazine	Water	0.30	0.0092
(2) Trifluralin	Water	0.0020	0.039
(3) DMDE	Water	0.30	0.094
(4) DMDE	Hexadecane	0.20	0.14
(5) DDE	Water	0.30	0.92
(6) Diphenylmercury	Water	0.27	0.80
(7) Phenylmercuric acetate	Water	0.25	1.6
(8) 2,4-D butoxyethyl ester	Hexadecane	0.17	3.8
(9) Carbaryl	Water	0.0060	6.6
(10) 2,4-D butoxyethyl ester	Water	0.056	12.0
(11) Benzo(f)quinoline	Water	0.014	0.060
(12) Dibenzo(e,g)carbazole	Water	0.0033	0.033
(13) Benzo(a)pyrene	Water	0.00089	0.059
(14) Benz (a)anthracene	Water	0.0033	0.066
(15) Carbazole	Water	0.0076	0.12
(16) Dibenzothiophene	Water	0.00050	5.7
(17) Quinoline	Water	0.00033	25.0
(18) Methyl parathion	Water	0.00017	9.0
(19) Parathion	Water	0.00015	10.0

(a) Half-life integrated over 24-hour day.
(b) Data from Zepp and Cline (9) and Smith *et al.* (5).

Influence of natural substances. As a first approximation in computing direct photolysis rates, we assume that the electronic absorption spectrum and quantum yield for reaction are the same in natural as in air-saturated pure water. How close is this assumed rate to the actual photolysis rate in a water body? In this section we discuss the likely effects of the dissolved and suspended matter in natural water upon direct photolysis.

Of course, if the pollutant rapidly undergoes a chemical reaction in a natural water that changes its chemical nature, then its photochemistry will change. Examples of such chemicals are certain phenols, such as pentachlorophenol, that dissociate to phenoxide ions in basic natural water. Also, the photoreactivity of other ionizable chemicals can be changed by complexation with natural species. For example, methylmercuric chloride, itself non-photoreactive, may be transformed into photoreactive sulfur-bonded complexes in some aquatic environments (Ref. 11). Likewise, NTA and EDTA (Refs. 12,13,14) become photoactivated when they form complexes with metal ions, such as iron (III), that are commonly found in lakes and rivers. Thus, to adequately forecast the photochemical behavior of ionizable chemicals, spectra and quantum yields of environmentally significant dissociated or complexed forms must be obtained.

Sorption of chemicals onto sediments in aquatic environments also has several important effects upon photolysis rates. Hautala has concluded that sorption of pesticides onto soil surfaces markedly diminishes their quantum yields for reaction (Ref. 15). The reaction

conditions in his experiments were considerably different from those found in natural waters, however. McGinnes reported that sorption onto a clay suspended in water had little effect on the direct photolysis rates of benzo[a]pyrene and benz[a]anthracene (Ref. 16). Recently, Miller examined the direct photolysis of several pesticides in the presence of sediments obtained from rivers and ponds in the southern United States (Ref. 17). He concluded that the effects of suspended sediments on the photochemical response of aquatic pollutants are likely to be unimportant compared to the diminution of the dose of sunlight caused by the presence of sediments (*vide infra*).

Dissolved species in natural water may alter quantum yields for reaction through interactions with the excited state, P*. "Quenching" interactions return the electronically excited pollutant to its ground state (eq. 7).

$$P^* + Q \xrightarrow{k_7} P_o \qquad (7)$$

The effect of quenchers upon the quantum yield for reaction is represented by the Stern-Volmer relation (eq 8).

$$\frac{\phi_o}{\phi_Q} = 1 + k_7 \tau_o [Q] \qquad (8)$$

where ϕ_o and ϕ_Q are the quantum yields in the absence and presence of quencher, respectively; k_7 is the rate constant for quenching; τ_o is the lifetime of P* in the absence of quencher; and [Q] is the concentration of quenchers (Ref. 18). Dissolved molecular oxygen is known to be an excellent quencher (Ref. 19), and because it is present at concentrations higher than other species in freshwater (Ref. 11), the quenching effect is adequately accounted for by simply conducting direct photolysis studies in air-saturated pure water. Excited state lifetimes of the pesticides, 2,4-D (Ref. 3) and methoxychlor (Ref. 8) are so short that their quantum yields should not be decreased by quenching in freshwaters. On the other hand, photoreactions of carbaryl (Ref. 6a) and probably polychlorinated biphenyls (PCB's) (Ref. 20) are partially quenched by oxygen in air-saturated water.

Interactions of P* with natural species may also involve chemical reaction (eq. 9).

$$P^* + Y \longrightarrow \text{Products} \qquad (9)$$

Direct photoreactions of polycyclic aromatics with oxygen are adequately simulated in air saturated pure water. Photoreactions with other species may increase the quantum yield for reaction, and thus the photolysis rate, over that observed in pure water and also may change the reaction products. For some time it has been known that certain aromatic compounds are susceptible to photoinduced nucleophilic substitution reactions (Ref. 21). Crosby and coworkers have provided ample evidence that many pesticides can undergo photonucleophilic reactions in the presence of high nucleophile concentrations (Ref. 22). Ruzo and coworkers have demonstrated that PCB's also undergo light-induced nucleophilic displacements (Ref. 20). Although nucleophilic species such as hydroxide, chloride, bromide, thiols, and sulfide are present in freshwater environments (Ref. 11), their concentrations are typically far too low for them to compete with nucleophilic displacements by water itself. Sea water, however,

may have sufficiently high concentrations of chloride (0.6 M) and bromide ($\sim 10^{-3}$ M) to compete with water.

In summary, because excited state lifetimes are very short (usually less than 10 nanoseconds) and because concentrations of chemical species are very dilute in aquatic environments, it is reasonable to assume that quantum yields for reaction are usually the same in pure, air-saturated water and natural water. Exceptions to this general rule may occur with some chemicals. Dissociation or complexation can, of course, alter the chemical nature, and thus, the photoreactivity of ionizable synthetic chemicals.

Sensitized Photolysis

Photosensitizers are chemicals that, upon light absorption, cause chemical changes that do not occur in their absence. That photosensitized oxidations occur in many biological systems has been known for some time (Refs. 18,23), but it was not demonstrated until very recently that photosensitized transformation of pesticides can occur on solid surfaces such as plant leaves (Ref. 24) or in aqueous solution (Refs. 3,6a,8,25,26,27). Pioneering studies by Crosby and Ross (25) demonstrated that ethylene thiourea, a pesticide metabolite, underwent photosensitized oxidation in water from an agricultural field, although it is inert to sunlight in distilled water. Zepp and coworkers have found that photosensitized transformations of a variety of pesticides occur in natural water (Refs. 3,6a,8,26). For example, the photochemical transformation of the insecticide, parathion, is greatly accelerated in water obtained from the Okefenokee Swamp in southern Georgia, U.S.A., and in many other natural waters as well (Fig. 3) (Ref. 28). In this section, we discuss several mechanisms that can account for these photosensitized transformations.

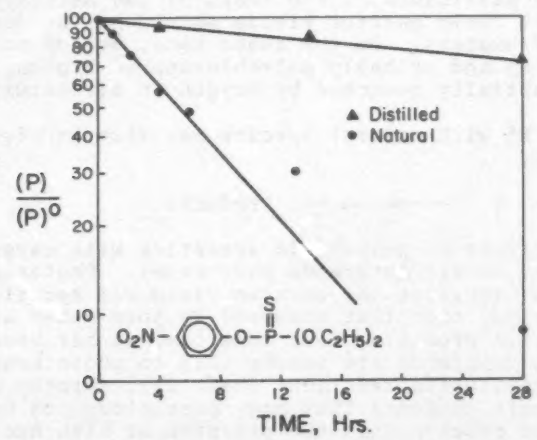


Fig. 3 Comparison of photolysis of parathion in distilled water and in a water sample obtained from the Aucilla River, Lamont, Florida

Energy transfer. One important mechanism involves the transfer of absorbed light energy from sensitizer to pollutant (eq. 10-14).

$$S + \text{Light} \longrightarrow {}^1S^* \quad (10)$$

$${}^1S^* \longrightarrow {}^3S^* \quad (11)$$

$${}^3S^* + P \xrightarrow{k_{12}} S + {}^3p^* \quad (12)$$

$${}^3S^* + O_2 \xrightarrow{k_{13}} S + O_2^* \quad (13)$$

$${}^3S^* \xrightarrow{k_{14}} S \quad (14)$$

Two systems of excited states are available to the sensitizer, the singlet, $^1S^*$, and triplet, $^3S^*$, states. Light absorption initially puts the sensitizer into its excited singlet state, but energy transfer usually occurs from the longer-lived triplet state, $^3S^*$. Under environmental conditions, most of the transferred energy goes to dissolved oxygen because the concentration of oxygen, an excellent energy acceptor, is typically several orders of magnitude greater than pollutant concentrations. The rate equation for a photosensitized reaction under environmental conditions is:

$$\text{Rate} = I_a^S \, \phi_{IS} \, \phi_{et} \, \phi_R \quad (15)$$

where I_a^S is the rate of light absorption by the sensitizer, ϕ_{IS} is the fraction of absorbed light that results in triplet formation, ϕ_R is the quantum yield for reaction of the pollutant, and ϕ_{et} is the fraction of triplet energy that is transferred from $^3S^*$ to the pollutant. The value of ϕ_{et} is:

$$\phi_{et} = \frac{k_{12}[P]}{k_{14} + k_{13}[O_2]} \quad (16)$$

where k_{12}, k_{13}, and k_{14} are rate constants for reactions 12-14, respectively, and $[O_2]$ is oxygen concentration. The maximum value of ϕ_{et} is the ratio of pollutant to oxygen concentration. Because oxygen concentrations are normally constant in the photic zone, sensitized photolysis, like direct photolysis, also obeys a first order rate expression.

Numerous studies have shown that the rate constant for triplet energy transfer (eq. 12) from a sensitizer is determined mainly by the energy of its lowest triplet state, not by its molecular structure (Ref. 18). Energy transfer occurs rapidly only when the triplet energy of the sensitizer equals or exceeds that of the energy acceptor. For example, the rate of photosensitized decomposition of phenylmercury fungicides is rapid with the high energy sensitizer, acetone, but very slow when sensitizers with lower triplet energies are employed (Ref. 29). Listed in Table 2 are triplet state energies of a variety of pesticides, pesticide derivatives, and other chemicals; in most cases the energies were computed from spectroscopic data in the literature.

The excited state energy of molecular oxygen is sufficiently low that triplet sensitizers that absorb uv and visible light transfer energy to it at the maximum rate. The product of energy transfer to oxygen is singlet oxygen, an excited form of oxygen that is a more powerful oxidizing species than ordinary oxygen (Ref. 18). Recently, the wavelength dependence, *i.e.* action spectrum, for generation of singlet oxygen was found to be strikingly similar in two natural water samples (Ref. 28) (Fig. 4). Because oxygen is the primary energy acceptor in natural waters, the curves in Fig. 4 also approximately represent the variation in efficiency of triplet sensitizer formation with wavelength. In view of what is known about dissolved matter in natural water, it is reasonable to assume that the sensitizers are principally complex, humic substances derived from plant decay (Refs. 30,31). The wavelengths of sunlight absorbed by the sensitizers (Fig. 4) correspond to triplet energies ranging from about 40 to 80 kcal/mole. Because the triplet state energies of many chemicals in Table 2 also fall in this range, photosensitized reaction via energy transfer may be an important transformation process. Energy transfer sensitization is more probable in the case of energy acceptors with lower triplet energies such as oxygen, polycyclic aromatics, parathion, carbaryl, and DDE. The low triplet energies of these compounds indicate that a wide range of sensitizers, including some that absorb visible light, can transfer energy to them.

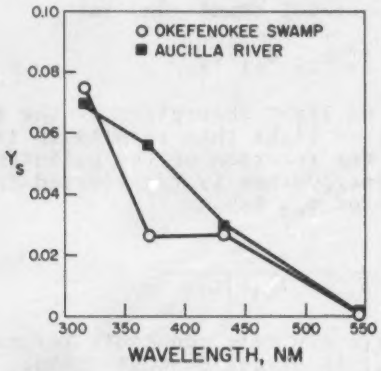


Fig. 4 Wavelength dependence of the quantum efficiency, Y_s, for photosensitized generation of singlet oxygen in samples from two water bodies

Several studies in the literature indicate that mechanisms other than energy transfer are also responsible for photosensitized decomposition. Ivie and Casida (24), for example, found a poor correlation between the effectiveness of several sensitizers and their triplet state energies. Moreover, Plimmer and Kearney (32) and Rosen and coworkers (33) have reported that chloroaniline decomposition is photosensitized by benzophenone and riboflavin. Because the triplet energies of benzophenone (68 kcal $mole^{-1}$) and riboflavin (47 kcal $mole^{-1}$) are lower than those of anilines (> 75 kcal $mole^{-1}$)(Table 2),

mechanism(s) other than energy transfer must account for these observations.

TABLE 2 Triplet State Energies of Selected Synthetic Chemicals (Refs. 6a,18)

Pesticide or related	Triplet Energy kcal/mole	Other	Triplet Energy kcal/mole
DDT	79	Benzene	85
Methoxychlor	80	Phenol	82
DDE	54	Aniline	77
DMDE	53	Acetone	80
Parathion	58	Benzophenone	69
Diazinon	76	Biphenyl	65
Carbaryl	60	Quinoline	62
2,4-D butoxyethyl ester	77	Naphthalene	61
p-Nitrophenol	58	Nitrobenzene	60
1-Naphthol	60	Chrysene	57
Hexachlorobenzene	70	Pyrene	49
		Riboflavin	47
		Benz (a)anthracene	47
		Anthracene	42
		Benzo(a)pyrene	42
		Naphthacene	29
		Oxygen	23

Chemical reaction. Another possible mechanism for photosensitization involves chemical reaction between the electronically excited sensitizer and the pollutant (eq. 17).

$$S^* + P \longrightarrow \text{Products} \qquad (17)$$

Of the variety of reactions that can occur, hydrogen atom transfer from pollutant to sensitizer is one of the most general (eq. 18).

$$S^* + P\text{-}H \longrightarrow SH^{\cdot} + P^{\cdot} \qquad (18)$$

In the presence of oxygen, this reaction can lead to oxidation of the pollutant by a free radical mechanism. The effectiveness of rotenone as a sensitizer (Ref. 24) is probably related to the fact that it is a substituted phenyl ketone; photoexcited phenyl ketones are known to be efficient hydrogen-atom abstractors (Ref. 34). Riboflavin, a widely used pesticide photosensitizer, is also a good hydrogen abstractor in the excited state (Ref. 35a). The riboflavin-sensitized oxidation of 2,4-dichlorophenol apparently involves hydrogen abstraction (Ref. 35b) as products resulting from coupling of free radicals are obtained.

Excited sensitizers such as ketones can form reactive excited-state complexes, or "exciplexes," with good electron donors (Refs. 36,37) such as alkyl amines (Ref. 38). Oxidation of the amine and reduction of the sensitizer occurs via electron transfer within the exciplex (eq. 19-21).

$$S^* + R_2NCH_2R \longrightarrow \underset{\text{Exciplex}}{(S^{\delta-}\cdots R_2N^{\delta+}CH_2R)^*} \qquad (19)$$

$$\text{Exciplex} \longrightarrow S^- + R_2\overset{+}{N}CH_2R \longrightarrow SH\cdot + R_2\dot{N}\dot{C}HR \qquad (20)$$

$$R_2\ddot{N}\dot{C}HR \xrightarrow[O_2]{H_2O} R_2NH + RCOH \qquad (21)$$

This mechanism may account for the acetone-sensitized dealkylation of triazine herbicides reported by Burkhard and Guth (39).

Photosensitized oxidation. The combination of light, oxygen, and natural photosensitizers in aquatic environments can lead to photooxidation of a wide variety of substances (Ref. 19). Two general types of sensitized photooxidations can occur (Ref. 40). Type I reactions are initiated by H-atom transfer (eq. 18) or electron transfer (eq. 20) followed by subsequent reaction of the resulting free radicals with oxygen or other chemical species. Type II reactions initially involve the previously mentioned interaction between triplet sensitizer and oxygen, usually to form singlet molecular oxygen (eq. 13). Reactions involving singlet oxygen are often called "oxygenations." The rates and chemistry of both types of reactions have been discussed in an excellent review by Foote (19), so emphasis here is on our findings concerning singlet oxygen in natural water (Ref. 41).

To obtain quantitative data that can be used to predict rates of photosensitized oxygenations, 2,5-dimethylfuran (DMF) was added to natural water samples to chemically snare the singlet oxygen. Although unreactive in distilled water, the DMF photooxidized in natural waters to form a hydroperoxide that, in turn, decomposed to *cis*-diacetylethylene and hydrogen peroxide (Fig. 5). That singlet oxygen, and not some other oxidizing species, was involved in the DMF oxidation was established by two mechanistic tests (Ref. 18). The photoreaction was accelerated upon addition of deuterium oxide to the natural water (Ref. 42), and it was slowed when DABCO, a singlet oxygen quencher, was added (Ref. 43). Studies employing monochromatic light (366 nm) established that singlet oxygen is photogenerated in a

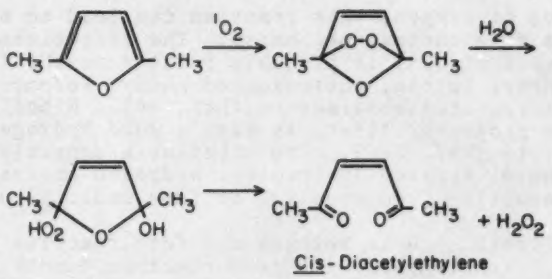


Fig. 5 Reaction of singlet oxygen with 2,5-dimethylfuran in water

wide variety of natural waters with a surprising uniformity of quantum efficiency, Y_S (Table 3). Steady-state concentrations of singlet oxygen [O_2*] were estimated from photooxygenation rates of DMF dissolved in natural water exposed to winter sunlight (Ref. 41). The concentrations of O_2* generated by sunlight were approximately proportional to the rate of generation of singlet oxygen at 366 nm, as reflected by the product of the fraction of light absorbed, F_{366}, and the quantum efficiency, Y_S, (Fig. 6). Because Y_S is relatively constant in these waters, the variation in [O_2*] was primarily governed by fraction absorbed. Figure 6 points out an important difference between direct and sensitized photolysis: Sensitized photolysis proceeds most rapidly in water bodies that are most opaque to sunlight, whereas the opposite is true of direct photolysis. That [O_2*] generated by exposure to sunlight correlated with the laboratory data obtained at a single wavelength suggests that the action spectra for photosensitized formation of O_2* must be similar in the natural waters that we examined. Indeed, we did find a striking similarity in the action spectra for the Okefenokee Swamp in south Georgia and the Aucilla River in north Florida (Fig. 4).

TABLE 3 Kinetic Parameters for Photochemical Generation of Singlet Oxygen in Natural Waters from the Southeastern United States (Ref. 41)

Water Body	pH	Total Organic Carbon, mg/l	F_{366} [a]	$(Y_s)_{366}$ [b]
Okefenokee Swamp, GA	4.1	24	0.389	0.056
Fenholloway River, Foley, FL	7.7	77	0.941	0.014
St. Marks River, St. Marks, FL	8.7	9	0.165	0.030
Gulf of Mexico, Shell Point, FL	8.5	6	0.050	0.060
Puddle in peanut field, Sylvester, GA	6.6	12	0.113	0.065
Mississippi River, Baton Rouge, LA	8.3	14	0.060	0.093
Average for 11 water bodies				0.043±0.019

(a) Fraction of 366-nm light absorbed in 1.00cm.
(b) Quantum efficiency for singlet oxygen formation at 366 nm.

Numerous rate data concerning reactions of singlet oxygen (eq. 22) are available in the chemical literature.

$$O_2^* + A \xrightarrow{k_A} AO_2 \qquad (22)$$

The half-lives for these photosensitized oxygenations equal 0.693 $(k_A[O_2^*])^{-1}$ (Ref. 41). Literature data concerning k_A values are translated in Table 4 into near-surface half-lives for photosensitized oxygenation of polycyclic aromatics (Ref. 44), biologically important substances (Ref. 45), and some pesticides. Photosensitized oxygenation of pesticides containing oxidizable moieties may also occur rapidly in natural water. A furan derivative, *cis*-resmethrin

(Ref. 46), must photooxidize about as rapidly as DMF. Moreover, Draper and Crosby (47) recently reported that disulfoton, a dialkyl sulfide, is photooxidized to disulfoton sulfoxide in a field water. Oxidation of sulfides is another known singlet oxygen reaction (Ref. 48).

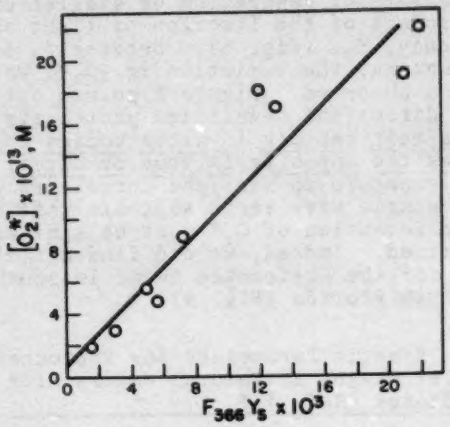
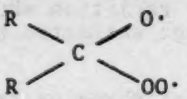


Fig. 6 Steady-state concentration of singlet oxygen generated by exposure of natural waters to sunlight versus laboratory data obtained using 366 nm; F_{366} and Y_S are fraction absorbed and quantum yield for singlet oxygen generation, respectively.

TABLE 4 Predicted Near-surface Half-lives for Photosensitized Oxidation of Selected Organics -- Mid-winter, Southern United States

	Half-life, hrs
Polycyclic Aromatics	
Benzo(a)pyrene	2500
7,12-Dimethylbenz(a)anthracene	6
Naphthacene	7
Pentacene	0.02
2,5-Dimethylfuran	0.20
Natural Chemicals	
Histidine	2
Tryptophan	2
Methionine	3
Methyl oleate	1100
Methyl linoleate	700
Pesticides	
cis-Resmethrin	0.2
Disulfoton	3

We should note that, although singlet oxygen does rapidly oxidize certain types of chemicals, it is a highly selective oxidizing species. Thus, many of the functional groups widely employed in pesticides are not readily oxygenated (Ref. 26). On the other hand, singlet oxygen may also play an indirect role in photooxidations. Peroxides formed by reactions between singlet oxygen and natural substances (Table 4) may serve as initiators for free radical oxidation (Ref. 6b). Draper and Crosby (47) and Ross and Crosby (25) have reported that peroxides were formed at low concentrations when samples from a variety of water bodies were exposed to sunlight. Ross and Crosby have suggested that these peroxides or "thermal oxidants" are involved in the photosensitized epoxidation of the insecticide, aldrin, to form dieldrin in a natural water (Ref. 49). Singlet oxygen is not directly involved in the reaction. More recently, Shimizu and Bartlett, in a detailed study of the photosensitized oxidation of olefins, suggested that the epoxidations may involve sensitizer-oxygen exciplexes or the biradical species shown below (Ref. 50).



Biological sensitization. Most of the above considerations concerned photosensitization in natural waters in which non-living humic material was the principal sunlight absorber. O'Kelley and Deason (51) recently discovered an interesting example of biologically mediated photodegradation (Fig. 7). The insecticide, malathion, is not degraded by the action of sunlight when dissolved in pure water (Ref. 6a). However, when aqueous solutions of malathion containing algae (either *Chlorella* sp. or *Nitzschia* sp.) were exposed to visible light, the malathion was rapidly converted to malathion monoacid. Control experiments showed that both light and algae were required for degradation to occur. These observations may be very significant, because algae are the principal sunlight absorbers in many clear lakes and the sea (Ref. 52).

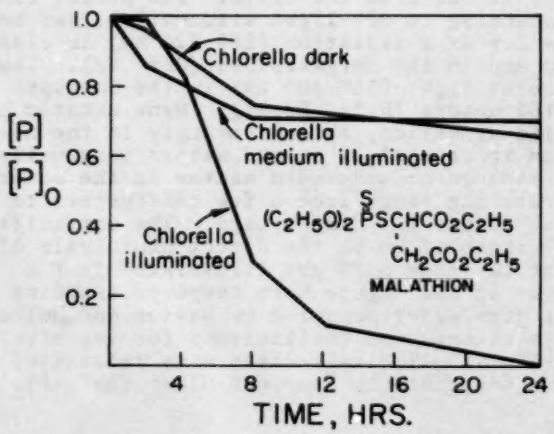


Fig. 7 Malathion degradation photosensitized by algae

LIGHT ATTENUATION AND PARTITIONING

One of the major uncertainties concerning photolysis rates in the aquatic environment has stemmed from lack of knowledge about the dose of light received by pollutants. In this portion, we discuss techniques for mathematically describing the effects of light attenuation and partitioning upon photolysis rates.

Light Attenuation

Much of what is known about the transmission of solar radiation in natural waters, including ultraviolet light, has been discussed in two excellent reviews (Refs.52,53). In the above discussion, the authors noted that uv and blue solar radiation is mainly responsible for photolysis of man-made chemicals. Most field measurements of underwater light have focused on visible radiation, because it is involved in photosynthesis and is easier to measure. More definitive data on transmission of uv radiation should soon be available, but until it is, only rough estimates based on laboratory data can be made.

Underwater light consists of three parts, direct light from the sun, diffuse light from the sky, and scattered light produced by interaction of light with suspended particles in the water. Light attenuation results from both absorption and scattering, but scattering is known to be less important than absorption in most natural waters. Miller found that suspended freshwater sediments attenuate middle uv radiation (280-340 nm) primarily through absorption (Ref. 16). Thus, as a first approximation, we have ignored scattering in assessing the effects of light attenuation on photolysis (Ref. 9).

Most observers are aware of the diversity in the optical properties of water bodies. Many lakes and the ocean are clear and blue, eutrophic lakes are often green because of suspended algae, and muddy rivers are brown and opaque. The popular belief that water, itself, strongly absorbs uv light, is far from the truth. The photic zone, defined as the depth corresponding to 99% light attenuation, has been shown to exceed 30 meters for uv-B radiation (280-320 nm) in clear ocean water near Puerto Rico and in the Sargasso Sea (Ref. 52). The photic zone for near ultraviolet light (350-400 nm) in the Sargasso Sea and Crater Lake is nearly 100 meters (Refs. 52,54). Many aquatic pollutants, such as polycyclic aromatics, absorb strongly in the near ultraviolet. Light attenuation in coastal or inland waters is usually caused almost completely by dissolved or suspended matter in the water. The photic zone in freshwaters can range from a few centimeters to the above-mentioned maximum values for Crater Lake. The variability in the effects of light attenuation on the direct photolysis of benzo[a]pyrene at latitude 50^{o}N are illustrated in Fig. 8. The average half-lives in the figure were computed assuming absorption coefficients for pure water measured by Dawson and Hulburt (55) and using the average attenuation coefficients for ten river waters in the southern U.S. (Ref. 9). The half-lives were calculated by computer using the program described by Zepp and Cline (Ref. 9).

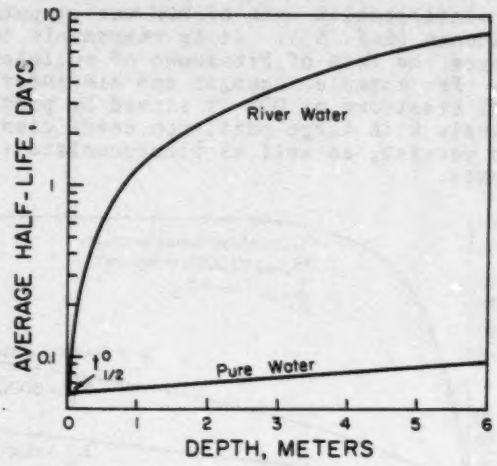


Fig. 8 Predicted average half-lives for photolysis of benzo(a)pyrene in water bodies of various depths (midsummer, latitude 50°N)

Effects of Partitioning

Considerations in the preceding section do not take into account the effects of partitioning to sediments. It is well known that certain hydrophobic pollutants such as DDT and benzo[a]pyrene have a great tendency to sorb to both suspended and bottom sediments. Because most of the sorbed pollutant is in the bottom sediment where no light is present, water-sediment partitioning decreases photolysis rates in aquatic environments. The tendency to sorb can be quantitatively described by the partition coefficient, K_p. The value of K_p is numerically equal to the weight ratio of sorbed to dissolved pollutant in a system that contains equal amounts of water and sediment. Figure 9 shows that the primary effect of suspended sediments on photolysis is the result of light attenuation, not partitioning. Typically, suspended sediment concentrations are 50 mg/liter or less (Ref. 16), and most pollutant in the water column is in the dissolved, not sorbed, form. Moreover, available evidence (Refs. 15,16) suggests that photolysis rates of sorbed and dissolved pollutant are similar.

To assess the effects of sorption to bottom sediment, equations shown in Fig. 10 were derived. The terms $[P_S]$ and $[P_W]$ represent concentrations of pollutants in sediments and water column, respectively, and C_S is the ratio of sediment to water. In deriving the equation, we assume that sediment-water exchange is much more rapid than transformation. If the pollutant is transformed much more slowly in the sediment than in the water column, *i.e.*, if $k_S \ll k_W$, then the observed photolysis rate is reduced by a factor of $(1 + K_pC_S)^{-1}$ relative to the rate in absence of partitioning. The value $(1 + K_pC_S)^{-1}$ incidentally, also corresponds to the fraction of pollutant in the water column. The computed effect of partitioning upon loss of DDE by photolysis and volatilization represents an extreme example

(Fig. 11). The volatilization rate of DDE was computed as described by Mackay and Leinonen (Ref. 56). It is reasonable to assume that partitioning changes the rate of breakdown of pollutants by other pathways as well. For example, Juengst and Alexander have suggested that the microbial breakdown of DDT is slowed by partitioning (Ref. 57). Thus, chemicals with large partition coefficients may have a great tendency to persist, as well as bioaccumulate (Ref. 58), in aquatic environments.

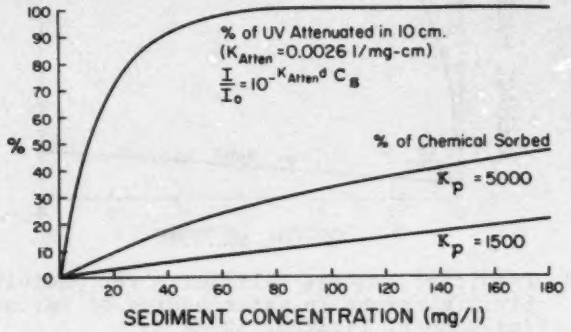


Fig. 9 UV light attenuation and sorption by suspended sediments. The terms, K_{Atten}, d, and C_s are attenuation coefficients, depth, and sediment concentration (mg/l), respectively; K_p is the sediment-water partition coefficient. Value of K_{Atten} is average for sediments obtained from five water bodies in Georgia, U.S.A. (Ref. 17)

$$\text{Products or Physical Loss} \xleftarrow{k_W} P_W \underset{}{\overset{K_P}{\rightleftharpoons}} P_S \xrightarrow{k_S} \text{Products}$$

$$K_P = \frac{[P_S]}{C_S [P_W]}$$

C_S = Sediment Concentration, g/l

$$[P_T] = [P_W] + [P_S]$$

$$-\frac{d[P_T]}{dt} = \frac{k_W + k_S C_S K_P}{1 + K_P C_S} [P_T]$$

$$\cong \frac{k_W}{1 + K_P C_S} [P_T] \quad \text{if } k_S \text{ is very low.}$$

Fig. 10 Equations describing effects of partitioning upon transformation

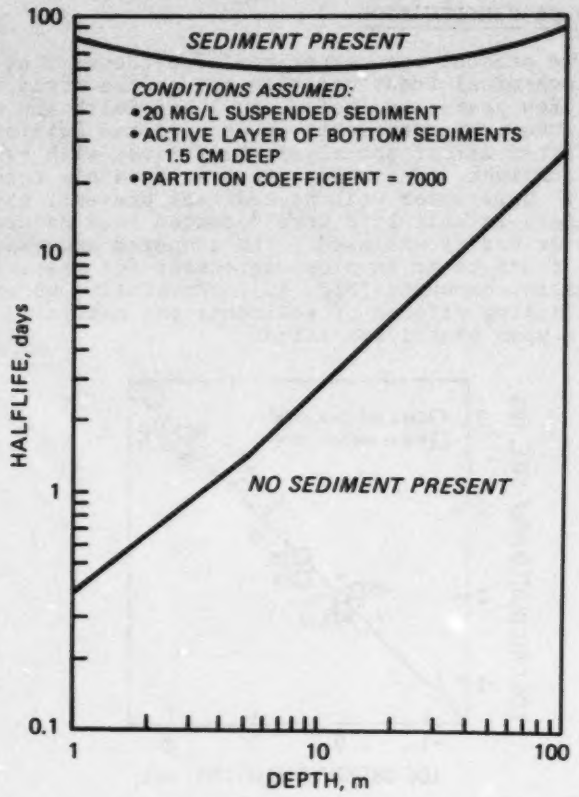


Fig. 11 Computed effects of partitioning upon photolysis and evaporative loss of DDE from water bodies of various depth

The possibility has also been suggested that accumulation of pollutants in surface films can accelerate photochemical transformation (Ref. 59). Analysis of slicks from the sea (Ref. 60) and the Great Lakes (Ref. 61) have confirmed that the concentrations of trace metals and chlorinated chemicals such as PCB's are 10- to 20-fold greater in the top 100 μm than in underlying water. Photolysis in surface films seems unimportant to us, however. Although the concentration of pollutant is higher in the surface film, the total amount of pollutant in the film is negligible compared to the amount even in just 1 meter of underlying water. This conclusion was also reached by Singmaster after more detailed study (Ref. 62).

OUTDOOR VERIFICATION

In conclusion, we present some experimental evidence that our attempts to predict photochemical transformation are on the right track. During the past few years, we (Refs. 6a,9) and Smith and coworkers (5) have conducted numerous experiments in Georgia and California designed to compare predicted direct photolysis half-lives with half-lives measured under sunlight. The experiments were mainly conducted at shallow depths in pure water with no sediment present, although no appreciable changes in half-life were detected when natural water from oligotrophic water bodies was used. The computed and experimental half-lives were found to be in close agreement for pesticides and polycyclic aromatic compounds (Fig. 12). Presently, we are developing methods for predicting effects of sediments and natural photosensitizers upon photolysis rates.

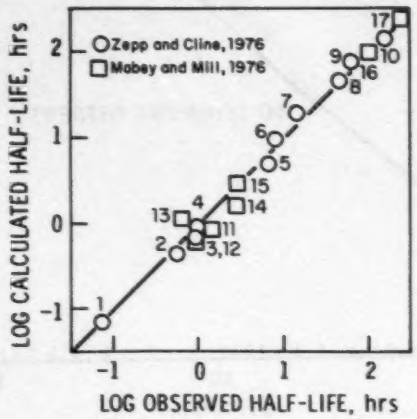


Fig. 12 Comparison of computed half-lives for direct photolysis of chemicals in water and half-lives measured at shallow depths under sunlight. The numbers correspond to chemicals listed in Table 1.

Usually, the behavior of a pollutant in a field situation is the result of a number of physical, chemical, and biological interactions. Modeling the behavior of a pollutant, however, is simplified when one or two processes are exceptionally rapid. For example, predicting the loss of vinyl chloride (Ref. 4) or chloroform (Ref. 63) from aquatic systems is greatly simplified by the dominance of volatilization. Laboratory data suggest that the major processes responsible for loss of DDE from the aquatic environment are photolysis and volatilization (Refs. 8,64) (Fig. 11). Experiments have shown that DDE is biodegraded very slowly (Refs. 1,65) and is chemically stable (Ref. 66). During June 1972, Hamelink and Waybrant (65) started a field study of the behavior of DDE in a large quarry in southern Indiana. Of particular interest to us was the unexplained loss of DDE from the quarry during the first year (Fig. 13). The initial rapid loss from the water column during the first 20 days was in part accounted for by

sorption to the bottom sediment. After this initial period, loss occurred much more slowly. Figure 13 shows the remarkable agreement between the observed concentration-time profile for DDE and the profile computed from laboratory data (Fig. 11) for a 15-meter-deep oligotrophic water body.

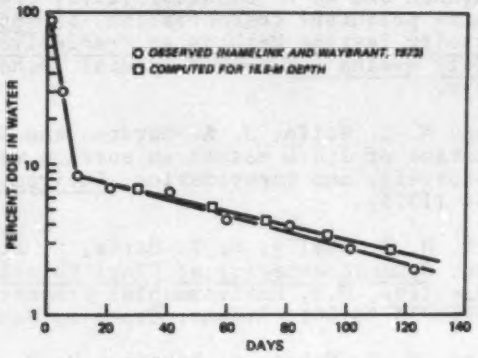


Fig. 13 Loss of DDE from the water column of an oligotrophic quarry at Oolitic, Indiana, during Summer 1972.

CONCLUSION

A technique is now available for using laboratory data to predict rates of direct photochemical reactions of aquatic pollutants. The technique allows estimates of the variations in photolysis rates as a function of location, time, and light attenuation in water bodies. Direct photolysis is likely to be an important pathway for transformation of chemicals such as pesticides, polycyclic aromatic hydrocarbons, and nitrosamines. Photolysis rates are expected to vary widely from one water body to another due to the effects of light attenuation and partitioning. The decrease in direct photolysis rates with increasing turbidity may be offset by an increase in rates of photosensitized reactions. Absorption of sunlight by natural photosensitizers can lead to transformation of chemicals that are photochemically inert in pure water. Thus, direct photolysis rates represent minimum values for rates of photochemical transformation in the aquatic environment.

ACKNOWLEDGEMENTS

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